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Applicants: Andrew B. Holmes *et al.*)

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For: Solution-Processable
Phosphorescent Materials

Group Art Unit: 1794

Examiner: Marie Rose Yamnitzky

Confirmation No. 8639

DECLARATION OF CHRISTOPHER KAY, Ph.D.
PURSUANT TO 37 C.F.R. §1.131

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Christopher Kay, Ph.D., hereby state as follows:

1.   I am authorized by Cambridge Enterprise Limited ("Cambridge"), the assignee of the above-identified patent application, to make this statement.

2.   I make this declaration for the purpose of providing evidence that, based on their activities in the United Kingdom, the inventors possessed at least as much as is shown in U.S. Patent Publication No. 2002/0193532 to Ikehira *et al.* at least as early as May 25, 2002 (the effective U.S. filing date of U.S. Patent Publication No. 2002/0193532 to Ikehira *et al.*), and subsequent to December 31, 1995.

3.   Submitted herewith as evidence of the inventors' possession of the at least as much as is shown in Ikehira *et al.* is a draft of a manuscript entitled "Solution-processable Triplet Emitters," which was completed at least as early as May 25, 2002, and subsequent to December 31, 1995. A copy of the draft manuscript is attached hereto as Attachment "A".

4.   Attachment A has been maintained as a business record in the normal course of business.

5.   The inventors' possession of at least as much as is disclosed in Ikehira *et al.* prior to the effective filing date of Ikehira *et al.* can be demonstrated, for example, by the description of the synthesis of materials R_2 and S_2 at pages 20 and 21, synthetic scheme 4 at page 45, and the description of the electroluminescent characteristics of organic light-emitting diodes (OLEDs) using materials R_2, S_2, and S_3 at page 32.

6.   I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. §1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: March 5, 2009   By: _Christopher P. Kay_

                                      Christopher Kay, Ph.D.

Solution-processable Triplet Emitters

Albertus J. Sandee, Nicholas E. Evans, Anna Köhler and Andrew B. Holmes

Contribution from the Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 9EW and the Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE

Abstract:

The synthesis and photophysical study of a series of solution-processable triplet emitters are reported. The novel *phosphors* are hybrid compounds of a bis cyclometalated iridium-2-phenylpyridinato complex (Ir(ppy)$_2$) triplet emitter, and polyfluorene, an efficient singlet emitting polymer. The series consists of Ir(ppy)$_2$(acac) complexes having fluorenyl substitutients on the 4-position of the ppy ligand. In the series, from non substituted complex Ir(ppy)$_2$(acac) (**L**) via monofluorenyl substituted complex [Ir(2-(6-p-pyridyl-phenyl)-9,9-dihexylfluorene)$_2$(acac)] (**N**) and the difluorenyl (Ir(2-(6-p-pyridyl-phenyl)-7-(9,9-dihexylfluorenyl)-9,9-dioctylfluorene)$_2$(acac)] (**O**) to the trifluorenyl [Ir(2-(6-p-pyridyl-phenyl)-7-(2-(7-[2-(9,9-dihexylfluorenyl)]))-9,9-dioctylfluorenyl)-9,9-dioctylfluorene)$_2$(acac)] (**P**) a major red-shift was observed in the PL-spectra of these complexes from 522 nm, via 552 nm and 561 to 566 nm. The polyfluorenyl substituted complex [Ir(ppy-pf8)$_2$(acac)] (**S$_2$**) also showed PL triplet emmision at 566 nm, along with minor singlet emmision at 445 nm. The red-shift of complex **N** with respect to **L** of 30 nm was found sufficient to complement the T$_1$ energy level of the

Attachment A

phosphor to that of polyfluorene; the EL spectrum of a blend of **N** in this polymer shows mainly triplet emission at 559 nm while the blend, containing complex **L** (λ_{max} at 535 nm), still shows substantial singlet emission at 441 nm. The stepwise elongation of the ppy ligand with fluorenyl segments resulted in a major increase in EL-brightness (from 60 for **L** to 1400 cd/m^2 for **P**) and in EL-quantum efficiency (from $7.4*10^{-4}$ to $7.3*10^{-2}$). Yellowish orange EL emission was obtained from S_2 (estimated fluorenyl length; 10 units) with a triplet to singlet ratio of 23:1 at a driving voltage of 7V, with a quantum efficiency of $7.9*10^{-2}$ and a maximum brightness of 163 cd/m^2. Upon increasing the length of the polyfluorene substituent to 30 (S_3) yielded whitish orange emmision having a triplet to singlet ratio of 7:1 (at 6V), with a quantum efficiency of $7.9*10^{-2}$ and a maximum brightness of 304 cd/m^2.

Introduction

Luminescent conjugated polymers are a new technologically important class of materials that will be used in light emitting display devices for the next generation of information technology based consumer products.[1,2] The principle interest in the use of polymers, as opposed to inorganic semiconducting and organic dye materials, lies in the scope for low-cost manufactoring, using solution-processing of film-forming materials.[3] Since the last decade much effort has been devoted to the improvement of the emission efficiency of organic light emitting diodes (OLED's)[4] either by developing highly efficient materials or efficient device structures.

In OLED's, electrons and holes are injected from opposite electrodes and are combined to form two types of excitons; spin-symmetric triplets and spin-antisymmetric singlets in a theoretical ratio of 3:1. Radiative decay from the singlets

is fast (fluorescence), but from the triplets (phosphorescence) it is formally forbidden by the requirement of the spin conservation. Initially spurred on by this understanding that the maximum internal quantum efficiency of an OLED was limited to 25% the idea of transferring both singlets and triplets to a phosphorescent dopant was conceived. Such a *phosphor* is able to accept both singlet and triplet excitons from the organic material and ideally generate electroluminescence from both. This idea is still highly applicable even given recent studies questioning the 3:1 triplet to singlet ratio predicted by the spin-independent recombination model.[5] Recent studies suggest that the proportion of triplet excitons generated in small molecule devices is indeed close to 75%,[6] whereas in an electrically excited conjugated polymer it is around 50%.[7,8] In the past few years many have studied the incorporation of phosphorescent materials into a semiconductive layer. Remarkable results have been achieved for OLED's based on small molecules, with internal quantum efficiencies as high as 87%.[9] Doped conjugated polymers have not been as successful, with only modest efficiencies reported so far.[10] One of the reasons for this is that blends of materials are sensitive to the concentration of the guest in the host, therefore even at relatively low concentrations the guest can phase separate leading to aggregation and luminescence quenching. It is recognised that this could be suppressed when the two components have similar surface functional groups[11] or when they are implemented in one composite material.[12]

The objective of the current study is to develop efficient phosphorescent materials that are easily solution-processible. This is accomplished by the attachment of subsequent fluorenyl segments to the 4-position of the ligand of a bis-cyclometalated iridium phosphor.[13] The energy levels of the novel phosphors are shown to be complementary to polyfluorene after having attached a monofluorenyl

substituent. It is shown furthermore that the stepwise addition of more fluorenyl segments to the phosphor gives rise to a gradual improvement of its performance as the emitting layer in an OLED device structure. The polyaddition to the phosphor was further extended towards the development of a polyfluorenyl-phosphor hybrid system.[14]

Experimental Section

Experimentals

General information

All reactions and manipulations were routinely performed under an argon or nitrogen atmosphere using standard Schlenk techniques or a glovebox. Acetonitrile and dichloromethane were distilled from CaH_2 and toluene and THF were distilled from Na prior to use. Water, glycerol, 2-ethoxyethanol and a 20% Et_4NOH solution in water were degassed for several h before use. All other reagents and chemicals were reagent grade and were used as received from commercial suppliers. Column chromatography was performed using silica gel [Merck 9385 Kieselgel 60 (230-400 ASTM]. TLC was performed on 0.25 mm thick plates precoated with Merck Kieselgel 60 F_{254} silica gel. ^{1}H NMR spectra were recorded on Bruker DPX-250 (250 MHz), Bruker DRX-400 (400 MHz) and Bruker DRX-500 (500 MHz) instruments using $CDCl_3$ or C_6D_6 as an internal deuterium lock. Chemical shifts are in ppm relative to TMS and are indicated as: s(singlet), d(doublet), tr(triplet), q(quartet), br(broad), m(multiplet), dd(double doublet), dtr(double triplet) etc. ^{13}C NMR spectra were recorded on Bruker DPX-250 (62.5 MHz) and Bruker DRX-400 (100 MHz) and a Bruker DRX-500 (121 MHz) instruments using an internal deuterium lock and proton decoupling. The multiplicity of the signal was determined by APT (Attached

Proton Test) experiments. Mass spectra were recorded by the Mass Spectrometry Services in the University of Swansea. Electron Impact (IE) and Chemical Ionisation (CI) low resolution spectra were carried out on a VG model 12-253 under ACE conditions. Accurate mass measurements for EI and CI were performed on a +VG ZAB-E instrument. Melting points were determined using a Büchi 510 melting point apparatus, and are uncorrected.

Synthesis of A (2(4-bromophenyl)pyridine)[15,16]

At 0°C, a solution of 16.84 g (244 mmol) $NaNO_2$ in 30 ml H_2O was slowly added to a suspension of 20 g (116.4 mmol) p-bromoaniline in 40 ml concentrated HCl. The resulting mixture was stirred for an h at below 5°C and was subsequently carefully poured in 500 ml pyridine. The resulting clear brown reaction mixture was stirred at 40°C for 4 h. 200 g of Na_2CO_3 was added to the mixture and the slurry was stirred for 18 h at 40°C. The organic layer was dissolved in dichloromethane, extracted with water and dried with $MgSO_4$. The crude product was purified by flash column chromatography (toluene:MeOH 95:5). Yield: 8.4 g (33%), conciderable yields of 7-(p-bromophenyl)pyridine were obtained as the major side product. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.68 (d, ^3J = 4.3 Hz, 1H; CH-N), 7.88 (d, ^3J = 8.4 Hz, 2H; CH-CH-Br), 7.75 (d, ^3J = 7.5 Hz, 1H; CH-CH-CH-N), 7.70 (d, ^3J = 7.8 Hz, 1H; CH-CH-CH-CH-N), 7.60 (d, ^3J = 8.4 Hz, 2H, CH-Br), 7.24 (br, 1H, CH-CH-N). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ = 156.2 (CN), 149.8 (CH-N), 138.3 (C-CN), 136.8 (CH-CH-CH-N), 131.9, 128.5 (Ar-CH), 123.4 (CBr), 122.4 (CH-CN), 120.2 (CH-CH-N). Exact Mass (IE) m/z: 233.9920 [M+H] (calcd. 233.9918 (^{79}Br)). $C_{11}H_8BrN$: calcd. C 56.44, H 3.44, N 5.98; found C 56.24, H 3.35, N 5.90.

Synthesis of **B** 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-7-trimethylsilyl-9,9-dioctylfluorene

At -78°C, 7.3 mL of a 1.7 M (12.5 mmol) tBuLi solution in hexanes was slowly added to a solution of 2.7 g (4.99 mmol) 2-bromo-7-trimethylsilyl-9,9-dioctylfluorene in THF. After 1 h, 1,2 g (6.48 mmol) of 2- isopropoxy-4,4,5,5 tetramethyl-1,3,2-dioxaborolane was added to the green solution at −78°C, after which the reaction mixture was allowed to warm up to roomtemperature. The resulting red solution turned colourless upon stirring for 18 h at roomtemperature. The product was extracted using dichloromethane/water and the crude product was purified by flash column chromatography (silica, 3% CDM in hexane). Yield 1.2 g (41%) product was obtained as colourless oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.80 (d, ^3J = 7.5 Hz, 1H; ArH), 7.75 (s, 1H; ArH), 7.70 (d, ^3J = 7.5 Hz, 2H; ArH), 7.48 (d, ^3J = 7.5 Hz, 1H; ArH), 7.46 (s, 1H, ArH), 1.97 (tr, 4H, ^3J = 8.3 Hz, CH$_2$-C$\underline{H}_2$-C), 1.39 (s, 12H, C$\underline{H}_3$-C(O)), 1.05-1.15 (mp, 20H, CH$_2$), 0,81 (t, ^3J = 7.1 Hz, 6H; C$\underline{H}_3$-CH$_2$), 0,61 (mp, 4H;CH$_2$), 0.31 (s, 9H, CH$_3$-Si). ^{13}C{^{1}H} NMR (500 MHz, CDCl3): δ = 150.4 ($\underline{C}$-C-CH$_2$), 150.1 ($\underline{C}$-C-CH$_2$), 144.1, 141.5, 139,6 (C), 133.6, 131.7, 128.9, 127.6, 119.3, 119.0 (CH), 83.7 (CO), 55.0 ($\underline{C}$-CH$_2$), 40.0 (C-$\underline{C}$H$_2$), 31.7, 30.0, 29.1, 29.0 (CH$_2$), 24.9 ($\underline{C}$H$_3$-CO), 23.6 (C-CH$_2$-$\underline{C}$H$_2$), 22.6 (CH$_3$-$\underline{C}$H$_2$), 14.0 ($\underline{C}$H$_3$-CH$_2$), 0.9 (CH$_3$-Si). Exact Mass (IE) m/z: 588.4534 (calcd 588.4534), fractions: 475.4 (m; [M-(C$_8$H$_{17}$)]$^+$, 363.3 (w; [M-(C$_8$H$_{17}$)$_2$]$^+$, 333.3 (m; [M-(C$_8$H$_{17}$+CH$_3$+C$_6$H$_{12}$BO$_2$)]$^+$). C$_{38}$H$_{71}$BO$_2$Si: calcd. C 77.52, H 10.44; found C 77.35, H 10.33.

Synthesis of C 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-7-bromo-9,9-dioctylfluorene

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At −78°C, 4.8 mL of a 1.6M (7.66 mmol) nBuLi solution in hexanes was slowly added to a solution of 4 g (7.30 mmol) of 2,7-dibromo-9,9-dioctylfluorene in 50 mL of diethylether. The resulting white milky solution was allowed to cool to 0°C until a clear-yellow solution was formed that was cooled back to −78°C again. 1.49 g (8.03 mmol) of 2- isopropoxy-4,4,5,5 tetramethyl-1,3,2-dioxaborolane was added and the resulting mixture turned white turbid after 1 h. The mixture was subsequently allowed to cool to roomtemperature and stirred for 18 h. After the mixture was quenched with water, the organic layer was dried on $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified using flash column chromatography (silica, dichloromethane, Rf: 0.5). Yield: 2.2 g (51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, ^3J = 7.6 Hz, 1H; ArH), 7.72 (s, 1H; ArH), 7.66 (d, ^3J = 7.5 Hz, 1H; ArH), 7.57 (d, ^3J = 7.5 Hz, 1H; ArH), 7.47 (s, 1H, ArH), 7.45 (d, ^3J = 7.5 Hz, 1H, ArH), 1.97 (mp, 2H, CH_2-CH_2-C), 1.91 (mp, 2H, CH_2-CH_2-C), 1.39 (s, 12H, CH_3-C(O)), 1.02-1.18 (mp, 20H, CH_2), 0,82 (t, ^3J = 7.1 Hz, 6H; CH_3-CH_2), 0,56 (mp, 4H;CH_2). ^{13}C{^{1}H} NMR (500 MHz, CDCl3): δ 153.3, 149.2 (C-C-CH_2), 142.7, 139.7 (ArC), 127.9 (very weak) (C-B), 133.6, 129.6, 128.6, 126.0, 121.2, 118.8 (CH), 83.5 (CO), 55.2 (C-CH_2), 39.9 (C-CH_2), 31.5, 29.6, 28.91, 28,88 (CH_2), 24.6 (C-CH_3), 23.4 (C-CH_2-CH_2), 22.3 (CH_2-CH_3), 13.8 (CH_2-CH_3). $C_{35}H_{52}BBrO_2$: calcd. C 70.59, H 8.80; found C 70.25, H 8.47.

Synthesis of **D** (2-(6-p-pyridyl-phenyl)-9,9-dihexylfluorene)

A mixture of 500 mg (1.12 mmol) of 2-(4,4,5,5,-tetramethyl-1,3,2,-dioxaboronate)-9,9-dihexylfluorene, 261 mg (1.12 mmol) of 2(4-bromophenyl)pyridine, 0.5 mg (0.01 mmol) $Pd(PPh_3)_4$, 2 ml of a 20% Et_4NOH in water in 4 ml toluene was stirred at 90°C for 18 h. The clear brown-orange mixture was taken in dichloromethane, washed with

water and finally dried with $MgSO_4$. The crude product was purified by flash column chromatography (DCM). Yield 255 mg (47%). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.73 (d, ^3J = 4.9 Hz, 1H; CH-N), 8.12 (d, ^3J = 8.2 Hz, 2H; C<u>H</u>-C-C(CH)-N), 7.80-7.78 (mp, 4H, ArH), 7.73 (d, ^3J = 7.8 Hz, 1H, C<u>H</u>-CH-CH-N), 7.64 (d, ^3J = 7.9, 1H; C<u>H</u>-CH-N), 7.62 (br, 1H; C<u>H</u>-CH-N), 7.36-7.33 (mp, ^3J = 1.0 Hz and 7.5 Hz, 3H; ArH), 7.25 (mp, 2H, ArH), 2.00-2.04 (dd, ^3J = 5.0 Hz and 5.2 Hz, 4H; C<u>H</u>$_2$-C), 1.05-1.15 (mp, 12H, CH_2), 0,78 (t, ^3J = 6.7 Hz, 6H; CH_3), 0,68 (mp, 4H;CH_2). $^{13}C\{^1H\}$ NMR (500 MHz, CDCl3): δ = 156.8 (CN), 151.2, 150.8 (<u>C</u>-C-CH_2), 149.5 (CH-N), 142.0, 140.5, 139.1, 137.8 (ArC), 136.5 (<u>C</u>H-CH-CH-N), 127.2, 127.0, 126.8, 126.5, 126.0, 122.7, 121.8, 121.1, 120.2, 119.7, 119.5 (CH), 54.9 (<u>C</u>-CH_2), 40.2 (C-<u>C</u>H_2), 31.2, 29.5 (CH_2), 23.5 (C-CH_2-<u>C</u>H_2), 22.3 (CH_3-<u>C</u>H_2), 13.7 (CH_3). Exact Mass (IE): 488.3317 [M+H] (calcd. 488.3317); fractions m/z: 402.3 (s, [M-(C_6H_{13})]$^+$):, 332.2 (s, [M-(C_6H_{13})-(C_5H_{11})]$^+$) 318.2 (s, [M-(C_6H_{13})$_2$]$^+$). $C_{36}H_{41}N$: calcd. C 88.65, H 8.47, N 2.87; found C 88.37, H 8.40, N 3.11.

Synthesis of E Suzuki polymerisation of 9,9-di-n-octylfluorene containing 2-(6-p-pyridyl-phenyl endgroup on one side

To a solution of 500 mg (0.56 mmol) of 2-(4,4,5,5,-tetramethyl-1,3,2,-dioxaboronate)-7-bromo-9,9-dioctylfluorene and 13.1 mg (0.056 mmol) 2-(6-p-pyridyl-phenyl in 5 ml toluene was added: 4 mg (0.004 mmol) Pd(PPh$_3$)$_4$ and 2.5 ml of a 20% (3.1 mmol) Et$_4$NOH solution in water. The resulting mixture was stirred for 24 h at 110°C. After the mixture was cooled down to 20°C the mixture was slowly transferred in a large excess of MeOH, allowing the polymer to precipitate as a yellow-white solid. The solids were collected on a filter, redissolved in 50 ml of toluene and subsequently filtered on a short column of silica. The filtrate was transferred into MeOH resulting

in a reprecipitation of the polymer as off-white fibres. The solvents were removed under reduced pressure. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.75 (br d, 2H*12%; CH-N), 8.13 (br d, 2H*12%, CH-CH-CH-N), 7.5-7.9 (br, 6H, ArH), 2.0-2.3 (br, 4H, CH$_2$-C), 1.0-1.3 (br, 20H, CH$_2$), 0.7-0.9 (br, 10H, CH$_3$+CH$_2$). Mw (NMR): 5000 (12-mer).

Synthesis of F 2-(6-p-pyridyl-phenyl)-7-trimethylsilyl-9,9-dioctylfluorene

To a solution of 243 mg (1.021 mmol) of (2(4-bromophenyl)pyridine), 600 mg (1.021 mmol) of 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-7-trimethylsilyl-9,9-dioctylfluorene in 10 mL of toluene was added: 4 mg (0.004 mmol) Pd(PPh$_3$)$_4$ and 2.5 ml of a 20 % (3.1 mmol) Et$_4$NOH solution in water. This two-phase reactionmixture was stirred for 48 h at 110°C after which it was extracted using dichloromethane/water. The organic layer was dried using MgSO$_4$ and the solvents were removed under reduced pressure. The crude product was purified using flash chromatography (dichloromethane, Rf: 0.47). 550 mg (88%) product was obtained as an off-white solid. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.73 (d, ^3J = 4.9 Hz, 1H; CH-N), 8.12 (d, ^3J = 8.3 Hz, 2H; CH-C-C(CH)-N), 7.80-7.78 (mp, 4H, ArH), 7.73 (d, ^3J = 4.5 Hz, 2H, CH-CH-CH-N), 7.69 (d, ^3J = 4.6 Hz, 2H; CH-CH-N), 7.63 (d, ^3J = 8.0 Hz, 2H; CH-CH-N), 7.25 (s, 1H; ArH), 2.01 (tr, ^3J = 8.2 Hz, 4H; CH$_2$-C), 1.05-1.15 (mp, 20H, CH$_2$), 0.78 (t, ^3J = 6.6 Hz, 6H; CH$_3$), 0.70 (mp, 4H;CH$_2$), 0.32 (s, 9H; CH$_3$-Si).

^{13}C{^{1}H} NMR (500 MHz, CDCl3): δ = 156.8 (CN), 151.5, 149.9 (C-C-CH$_2$), 149.5 (CH-N), 142.0, 141.1, 140.4, 139.2, 138.9, 137.8 (ArC), 136.5 (CH-CH-CH-N), 131.6, 127.4, 127.2, 127.0, 125.7, 121.8, 121.2, 120.1, 119.8, 118.8 (CH), 54.9 (C-CH$_2$), 39.9 (C-CH$_2$), 31.5, 28.9, 28.8 (CH$_2$), 29.7 (C-CH$_2$-CH$_2$-CH$_2$) 23.5 (C-CH$_2$-CH$_2$), 22.3 (CH$_3$-CH$_2$), 13.8 (CH$_2$-CH$_3$), −1.1 (Si-CH$_3$). Exact Mass (IE): [M+H]:

616.4340 (calcd. 616.4338). $C_{43}H_{57}NSi$: calcd. C 83.84, H 9.33, N 2.27; found C 83.99, H 9.41, N 2.33.

Synthesis of G 2-(6-p-pyridyl-phenyl)-7-iodo-9,9-dioctylfluorene

1.5 ml of an 1.0 M ICl solution in MeOH was slowly added to a solution of 500 mg (0.813 mmol) of 2-(6-p-pyridyl-phenyl)-7-trimethylsilyl-9,9-dioctylfluorene in 5 mL of dichloromethane. The resulting darkred solution was stirred for 2 h at roomtemperature after which the reactionmixture was quenched with a large excess of a $Na_2S_2O_3$ in water. The mixture was extracted with water, and the organic fraction was dried using $MgSO_4$ and the solvents were removed under reduced pressure. The product was purified using flash column chromatography (dichloromethane: Rf: 0.36). 450 mg (85%) product was obtained as a highly blue fluorescent, colourless solid material. ^1H NMR (250 MHz, CDCl$_3$): δ = 8.73 (d, ^3J = 4.7 Hz, 1H; CH-N), 8.12 (d, ^3J = 8.5 Hz, 2H; CH-C-C(CH)-N), 7.80-7.73 (mp, 4H, ArH), 7.68 (s, 2H, ArH), 7.65 (d, ^3J = 5.0 Hz, 2H; CH-CH-N), 7.60 (s, 2H; ArH), 7.48 (d, 1H; ^3J = 8.4 Hz; ArH), 2.05-1.94 (mp, 4H;CH$_2$-C), 1.05-1.25 (mp, 20H, CH$_2$), 0.81 (t, ^3J = 6.6 Hz, 6H; CH$_3$), 0.70 (br m, 4H, CH$_2$). $^{13}C\{^1H\}$ NMR (500 MHz, CDCl3): δ = 157.0 (CN), 153.4, 150.9 (C-C-CH$_2$), 149.8 (CH-N), 142.0, 140.4, 140.0, 139.6, 138.2 (ArC), 136.8 (CH-CH-CH-N), 135.9, 132.1 (C-CI), 127.5, 127.3, 126.1, 122.1, 121.5, 121.3, 120.4, 120.1 (CH), 92.6 (CI), 55.5 (C-CH$_2$), 40.2 (C-CH$_2$), 31.7, 29.9, 29.2, 29.1 (CH$_2$), 23.7 (C-CH$_2$-CH$_2$), 22.6 (CH$_3$-CH$_2$), 14.1 (CH$_3$). Exact Mass (IE) m/z: 669.2825 [M]$^+$ (calcd. 669.2832) fractions: 543.6 (m; [M-I]$^+$), 318.4 (m; [M-(C$_8$H$_{17}$)-I]$^+$). $C_{40}H_{48}IN$: calcd. C 71.74, H 7.22, N 2.09; found C 72.34, H 7.20, N 2.12.

Synthesis of H 2-(6-p-pyridyl-phenyl)-7-(9,9-dihexylfluorenyl)-9,9-dioctylfluorene

To a solution of 400 mg (0.60 mmol) of 2-(6-p-pyridyl-phenyl)-7-iodo-9,9-dioctylfluorene, 362 mg (0.60 mmol) of 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-9,9-dihexylfluorene in 10 mL of toluene was added: 4 mg (0.004 mmol) $Pd(PPh_3)_4$ and 2.5 ml of an 20 % (3.1 mmol) Et_4NOH solution in water. This two-phase reactionmixture was stirred for 48 h at 110°C after which it was extracted using dichloromethane/water. The organic layer was dried on $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified using flash chromatography. Yield 450 mg (86%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, ^3J = 4.9 Hz, 1H; CH-N), 8.13 (d, ^3J = 4.6 Hz, 2H; CH-C-C(CH)-N), 7.84-7.77 (mp, 6H, ArH), 7.74 (d, ^3J = 6.0 Hz, 2H, CH-CH-CH-N), 7.69-7.63 (mp, 6H; ArH), 7.39-7.30 (mp, 3H; ArH), 7-27-7.24 (mp, 1H (obscured by $CDCl_3$ peak ; ArH), 2.11-2.02 (mp, 8H, C-CH_2), 1.18-1.09 (mp, 32H, CH_2), 0.81-0.74 (mp, 20H, CH_2-CH_3). $^{13}C\{^1H\}$ NMR (500 MHz, CDCl3): δ = 157.1 (CN), 151.8, 151.4, 151.0 (C-C-CH_2), 149.8 (CH-N), 142.2, 140.8, 140.6, 140.42, 140.39, 140.3, 139.9, 139.3, 138.1 (ArC), 136.8 (CH-CH-CH-N), 127.5, 127.3, 126.9, 126.8, 126.1, 126.0, 122.1, 122.0, 121.44, 121.38, 120.4, 120.0, 119.8, 119.7 (CH), 55.3, 55.1 (C-CH_2), 40.4 (C-CH_2), 31.7, 31.5, 30.0, 29.7, 29.18, 29.16 (CH_2), 23.8, 23.7 (C-CH_2-CH_2), 22.6, 22.5 (CH_3-CH_2), 14.03, 13.99 (CH_3). Exact Mass (IE): 875.6367 $[M]^+$ (calcd 875.6369) fractions m/z:: 762.3 (m; $[M-(C_8H_{17})]^+$, 650.4 (m; $[M-(C_8H_{17})_2]^+$. $C_{65}H_{81}N$: calcd. C 89.09, H 9.32, N 1.60; found: C 88.60, H 9.25, N 1.52.

Synthesis of **J** (via **I**) 2-(6-p-pyridyl-phenyl)-7-(2-(7-iodo-9,9-dioctylfluorenyl)-9,9-dioctylfluorene

To a solution of 300 mg (0.448 mmol) of 2-(6-p-pyridyl-phenyl)-7-iodo-9,9-dioctylfluorene, 320 mg (0.544 mmol) of 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-7-trimethylsilyl-9,9-dioctylfluorene in 10 mL of toluene was added: 4 mg (0.004 mmol) $Pd(PPh_3)_4$ and 2.5 ml of a 20 % (3.1 mmol) Et_4NOH solution in water. This two-phase reactionmixture was stirred for 24 h at 110°C after which it was extracted using dichloromethane/water. The organic layer was dried and the solvents were removed under reduced pressure. The crude product was purified using flash chromatography (dichloromethane, Rf: 0.30). 392 mg (88%) of product **I** was obtained as a colourless solid. This was subsequetly dissolved in 5 ml of dichloromethane and 5 mL of 1.0 M solution of ICl in MeOH was added. The resulting darkred solution was stirred for 2 h at roomtemperature after which the reactionmixture was queched with a large excess of a $Na_2S_2O_3$ solution in water. The reactionmixture was subsequently extracted (dichloromethane/water). The organic phase was dried on $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified using column chromatography (silica, dichloromethane). Yield: 355 mg (85%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, ^3J = 4.6 Hz, 1H; CH-N), 8.13 (d, ^3J = 8.4 Hz, 2H; C<u>H</u>-C-C(CH)-N), 7.82-7.78 (mp, 5H, ArH), 7.75 (d, ^3J = 7.9 Hz, 2H, C<u>H</u>-CH-CH-N), 7.69-7.64 (mp, 5H; ArH), 7.60 (d, 2H; ArH), 7.48 (d, 1H; C<u>H</u>-CH-N) 7.26-7.24 (mp, 2H (obscured by $CDCl_3$ peak ; ArH), 2.17-1.94 (mp, 8H, C-CH_2), 1.24-1.09 (mp, 40H, CH_2), 0.90-0.71 (mp, 20H, C<u>H</u>_2-C<u>H</u>_3). $^{13}C\{^1H\}$ NMR (500 MHz, CDCl3): δ = 157.0 (CN), 153.4, 151.83, 151.77, 150.9 (<u>C</u>-C-CH_2), 149.8 (CH-N), 142.1, 141.1, 140.5, 140.4, 140.3, 140.1, 139.4, 139.3, 138.1 (ArC), 136.8 (<u>C</u>H-CH-CH-N), 135.9, 132.1 (<u>C</u>-CI), 127.5, 127.3,

126.24, 126.16, 126.1, 122.1, 121.4, 121.3, 120.4, 120.1, 120.0 (CH, 3 CH signals obscured by exact overlap), 92.5 (CI), 55.5, 55.3 (C-CH$_2$), 40.4, 40.2 (C-CH$_2$), 31.77, 31.76, 29.19, 29.17 (CH$_2$), 29.99, 29.93 (C-CH$_2$-CH$_2$-CH$_2$) 23.8, 23.7 (C-CH$_2$-CH$_2$), 22.60, 22.58 (CH$_3$-CH$_2$), 14.08, 14.05 (CH$_3$). Exact Mass (IE): [M+H] (calcd.); fractions m/z: 1058.7 (s, [M]$^+$), 944.4 (m, [M-(C$_8$H$_{17}$)]$^+$. C$_{69}$H$_{88}$IN: calcd. C 78.30, H 8.38, N 1.32; found. C 78.02, H 8.31, N 1.35.

Synthesis of K 2-(6-p-pyridyl-phenyl)-7-(2-(7-[2-(9,9-dihexylfluorenyl)]))-9,9-dioctylfluorenyl)-9,9-dioctylfluorene

To a solution of 300 mg (0.287 mmol) of 2-(6-p-pyridyl-phenyl)-7-(2-(7-iodo-9,9-dioctylfluorenyl)-9,9-dioctylfluorene, 225 mg (0.373 mmol) of 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-7-trimethylsilyl-9,9-dioctylfluorene in 5 mL of toluene was added: 4 mg (0.004 mmol) Pd(PPh$_3$)$_4$ and 2.5 ml of a ?% (3.1 mmol) Et$_4$NOH solution in water. This two-phase reactionmixture was stirred for 24 h at 110°C after which it was extracted using dichloromethane/water. The organic layer was dried and the solvents were removed under reduced pressure. The crude product was purified using flash chromatography (silica/dichloromethane:hexane 1:1, Rf: 0.24). Yield: 190 mg (52%) of a colourless, highly blue fluorescent solid. %). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.75 (d, ^3J = 4.6 Hz, 1H; CH-N), 8.14 (d, ^3J = 8.4 Hz, 2H; CH-C-C(CH)-N), 7.86-7.73 (mp, 10H, ArH), 7.74-7.62 (mp, 10H, ArH), 7.40-7.31 (mp, 3H, ArH), 7.28-7.23 (mp, 1H (obscured by CDCl$_3$), ArH), 2.17-2.02 (mp, 12H, C-CH$_2$), 1.25-1.01 (mp, 52H, CH$_2$), 0.90-0.64 (mp, 30H, CH$_2$-CH$_3$).

^{13}C{^{1}H} NMR (500 MHz, CDCl3): δ = 157.1 (CN), 151.8, 151.4, 151.0 (C-C-CH$_2$), 149.7 (CH-N), 142.2, 140.8, 140.6, 140.5, 140.47, 140.44, 140.39, 140.30, 139.95,

139.90 (ArC), 136.7 (CH-CH-CH-N), 127.4, 127.3, 126.8, 126.1, 126.0, 122.9, 121.44, 121.40, 120.38, 120.0, 119.9, 119.8, 119.7 (CH), 55.33, 55.31, 55.1 (C-CH$_2$), 40.3 (C-CH$_2$), 31.7, 31.4, 30.0, 29.7, 29.2 (CH$_2$), 23.9, 23.8 (C-CH$_2$-CH$_2$), 22.6, 22.5 (CH$_3$-CH$_2$), 14.01, 13.97 (CH$_3$). Mass (IE) m/z; 1265 [M+H]$^+$. C$_{94}$H$_{121}$N: calcd. C 89.25, H 9.64, N 1.11; found C 89.25, H 9.71, N 1.21.

Synthesis of [Ir(2(4-bromophenyl)pyridine)$_2$μ-Cl]$_2$[17]

A mixture of 500 mg (1.42 mmol Ir) IrCl$_3$.xH$_2$O and 1.4 g (6.37 mmol) of 2(4-bromophenyl)pyridine in 50 ml 2-ethoxyethanol and 15 ml H$_2$O was heated to 110°C for 18h. A yellow precipitate started to form after 1h. After the mixture was allowed to cool down to 20°C, the precipitate was collected on a fritted glass filter, washed with EtOH:H$_2$O 95:5, dissolved in acetone and dried on MgSO$_4$. The solvent was removed under reduced pressure. Yield 639 mg (65%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 9.12 (d, ^3J = 5.7 Hz, 4H; CH-N), 7.86 (d, ^3J = 4.5 Hz, 4H; CH-CH-CBr), 7.80 (dtr, ^4J = 1.5 Hz and ^3J = 7.2 Hz, 4H; CH-CH-Br), 7.38 (d, ^3J = 9.4 Hz, 4H; CH-CH-CH-N), 7.02 (dd, ^3J = 1.9 Hz and 9.0 Hz, 4H; CH-C(C)N), 6.84 (dtr, ^4J = 1.7 Hz and ^3J = 5.6 Hz, 4H; CH-CH-N), 5.94 (d, ^4J = 1.9 Hz, 4H; CH-C(C)-Ir). Mass (FAB): m/z 1387 (w, [M]$^+$), 1352, (w, [M-Cl]$^+$), 659 (s, [Ir(A)$_2$]$^+$). C$_{44}$H$_{32}$Br$_4$Cl$_2$Ir$_2$N$_4$: calcd. C 38.08, H 2.03, N 4.04; found C 37.73, H 2.10, N 4.04.

Synthesis of M (Ir(2(4-bromophenyl)pyridine)$_2$acac)[18]

300 mg (0.216 mmol) of [Ir(2(4-bromophenyl)pyridine)$_2$μ-Cl]$_2$ was dissolved in 30 ml 2-ethoxyethanol in the presence of 108 mg (1.08 mmol) acacH and 216 mg (2.04 mmol) Na$_2$CO$_3$. The resulting yellow suspension was stirred at 110°C for 8h. After

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the mixture was allowed to cool down to 20°C 10 ml of H_2O was added. The yellow precipitate was collected on a fritted glass filter, washed with H_2O, hexane and with cold Et_2O, and dried under reduced pressure. Yield: 190 mg (58%). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.44 (d, ^3J = 5.5 Hz, 2H; CH-N), 7.83 (d, ^3J = 8.5 Hz, 2H, CH-CH-CH-N), 7.78 (mp, ^3J = 5.5 Hz and ^4J = 1.5 Hz, 2H; CH-CH-N), 7.41 (d, ^3J = 8.3 Hz, 2H; CH-CH-CH-CH-N), 7.19 (dtr, ^3J = 6.4 Hz and ^4J = 1.5 Hz, 2H, ArH), 7.00 (dd, ^3J = 6.3 Hz and ^4J = 2 Hz, 2H; ArH), 6.28 (d, ^4J = 2Hz, 2H; CH-C(C)-Ir), 5.23 (s, 1H; CH-C=O), 1.79 (s, 6H; CH_3). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ = 184.8 (CO), 167.5 (CN), 148.2 (CH-N), 143.8 (C-Ir), 137.3, 135.4 (ArC), 125.1, 124.1, 121.9, 118.7 (Ar-CH), 100.5 (CH-CO), 28.6 (CH_3-CO). Exact Mass (IE): 755.9593 (calcd. 755.9599 for $[M]^+$ with $(^{193}Ir)(^{79}Br)$); m/z: 658.8 (s, $[M$-acac$]^+$), 579.0 (m, $[M$-acac-Br$]^+$, 499 (w, $[M$-acac-$(Br)_2]^+$. $C_{27}H_{21}Br_2IrN_2O_2.H_2O$: calcd. C 41.82, H 2.99, N 3.61; found C 42.02, H 2.60, N 3.54.

Synthesis of $[Ir(2-(6-p-pyridyl-phenyl)-9,9-dihexylfluorene)_2\mu-Cl]_2$

Synthetic route is analogous to synthesis of $[Ir(2(4-bromophenyl)pyridine)_2\mu-Cl]_2$. Yield: 66%. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.45 (d, ^3J = 5.4 Hz, 4H; CH-N), 7.95 (d, ^3J = 7.2 Hz, 4H; CH-C-C(CH)-N), 7.80 (t, ^3J = 7.2 Hz, 4H; CH-CH-C-C(CH)-N), 7.63 (br, 4H; CH-CH-CH-N), 7.56 (mp, ^3J = 6.7 Hz, 4H; CH-C-N), 7.26 (br mp, 20H; ArH), 7.12 (s, 4H; FlH), 7.10 (mp, 4H, FlH), 6.89 (t, ^3J = 5.4 Hz, 4H; CH-CH-N), 6.35 (s, 4H; CH-CIr), 1.7-2.0 (br mp, 16H; CH_2-C), 0.9-1.2 (br mp, 48H, CH_2), 0,78 (br mp, 24H; CH_3), 0,4-0.6 (br, 16H;CH_2).

Synthesis of N $(Ir(2-(6-p-pyridyl-phenyl)-9,9-dihexylfluorene)_2(acac))$

Synthetic route is analogous to synthesis of **M**. Yield: 78%. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.63 (d, ^3J = 5.7 Hz, 2H; CH-N), 7.92 (d, ^3J = 7.9 Hz, 2H; C$\underline{\text{H}}$-C-C-N), 7.76 (tr, ^3J = 7.2 Hz and ^4J = 1.4 Hz, 2H; ArH), 7.64 (d, ^3J = 6.0 Hz, 2H; ArH), 7.58 (d, ^3J = 5.9 Hz, 2H; ArH), 7.2-7.3 (br mp, ^3J = 8.0 Hz, 12H; ArH), 7.1-7.2 (mp, ^3J = 7.1 Hz, 4H; ArH), 6.59 (s, 2H, CH-CIr), 1.8-2.0 (br, 8H; CH$_2$-C), 0.9-1.2 (br mp, 24H, CH$_2$), 0,77 (mp, 12H; CH$_3$), 0,4-0.6 (br, 8H;CH$_2$). ^{13}C{^{1}H} NMR (500 MHz, CDCl3): δ = 184.7 (CO), 168.5 (CN), 150.8, 150.6 ($\underline{\text{C}}$-C-CH$_2$), 148.4 (CH-N), 144.0 (C-Ir), 141.4, 140.9, 140.4, 139.9 (ArC), 136.7 ($\underline{\text{C}}$H-CH-CH-N), 126.7, 126.6, 125.8, 124.0, 122.7, 121.4, 121.3, 121.1, 120.0, 119.5, 119.3, 118.4 (CH), 100.4 ($\underline{\text{C}}$H-CO), 54.9 ($\underline{\text{C}}$-CH$_2$), 40.53, 40.48 (C-$\underline{\text{C}}$H$_2$), 31.5, 29.8 (CH$_2$), 28.8 ($\underline{\text{C}}$H$_3$-CO), 23.6 (C-CH$_2$-$\underline{\text{C}}$H$_2$), 22.6 (CH$_3$-$\underline{\text{C}}$H$_2$), 14.0, 13.9 (CH$_3$). Mass (EI) m/z: 1178.3 (w, [M-(C$_6$H$_{13}$)]$^+$, 1165.2 (s, [M-(acac)]$^+$, 1009 (m, [M-(C$_6$H$_{13}$)$_3$]$^+$). C$_{77}$H$_{87}$IrN$_2$O$_2$.H$_2$O: calcd. C 72.10, H 6.99, N 2.18; found C 72.40, H 6.87, N 2.27.

Synthesis of **O** (Ir(2-(6-p-pyridyl-phenyl)-7-(9,9-dihexylfluorenyl)-9,9-dioctylfluorene)$_2$(acac)). Synthetic route is analogous to synthesis of **N** with some minor alterations. The dichlorobridged diiridiumcomplex was prepared in 2-ethoxyethanol and precipitated by adding water. Yield: 59%. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.65 (d, ^3J = 5.1 Hz, 2H; CH-N), 7.86 (d, ^3J = 7.8 Hz, 2H; C$\underline{\text{H}}$-C-C-N), 7.75-7.58 (mp, 24H; ArH), 7.37-7.16 (mp, 10H; ArH), 6.61 (s, 2H; C$\underline{\text{H}}$-CH-N), 5.27 (s, 1H; CH-CO), 2.03-1.94 (mp, 16H; C-C$\underline{\text{H}}_2$), 1.85 (s, 6H, CH$_3$-CO), 1.32-0.91 (mp, 64H, CH$_2$), 0.88-0.70 (mp, 40H, C$\underline{\text{H}}_2$-C$\underline{\text{H}}_3$). ^{13}C{^{1}H} NMR (500 MHz, CDCl3): δ = 184.7 (CO), 168.5 (CN), 151.6, 151.4, 151.00, 150.97 ($\underline{\text{C}}$-C-CH$_2$), 148.4 (CH-N), 144.1 (C-Ir), 141.5, 140.8, 140.5, 140.2, 139.6 (ArC), 136.7 ($\underline{\text{C}}$H-CH-CH-N), 126.9, 126.7, 126.0, 125.9, 124.0, 122.9, 121.5, 121.34, 121.29, 119.8, 119.7, 119.4, 118.4

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(CH), 100.8 (C̲H-CO), 55.1, 55.0 (C̲-CH$_2$), 40.6, 40.5, 40.3 (C-C̲H$_2$), 31.78, 31.77, 31.4, 30.2, 29.7, 29.3, 29.2 (CH$_2$), 28.8 (C̲H$_3$-CO), 23.7 (C-CH$_2$-C̲H$_2$), 22.58, 22.57, 22.54 (CH$_3$-C̲H$_2$), 14.06, 13.99 (CH$_3$). Mass (IE) m/z: 2041.4 (s, [M]$^+$), 1942.4 (m, [M–(acac)]$^+$ C$_{135}$H$_{167}$IrN$_2$O$_2$: calcd. C 79.40, H 8.24, N 1.37; found C 79.12, H 8.13, N 1.17.

Synthesis of **P** (Ir(2-(6-p-pyridyl-phenyl)-7-(2-(7-[2-(9,9-dihexylfluorenyl)]))-9,9-dioctylfluorenyl)-9,9-dioctylfluorene)$_2$(acac)). Synthetic route is analogous to synthesis of N. Yield: 57%. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.65 (d, ^3J = 5.4 Hz, 2H; CH-N), 7.94 (d, ^3J = 8.3 Hz, 2H; C̲H-C-C-N), 7.82-7.78 (mp, 8H; ArH), 7.75-7.72 (t, ^3J = 8.2 Hz, 4H; ArH), 7.67-7.63 (mp, 22H; ArH), 7.38-7.31 (mp, 8H; ArH), 7.21-7.17 (mp, 4H; ArH), 6.61 (s, 2H; C̲H-CH-N), 5.28 (s, 1H; CH-CO), 2.11-2.02 (mp, 24H; C-C̲H$_2$), 1.85 (s, 6H, CH$_3$-CO), 1.20-1.07 (mp, 104H, CH$_2$), 0.82-0.67 (mp, 60H, C̲H$_2$-C̲H$_3$). ^{13}C{^{1}H} NMR (500 MHz, CDCl3): δ = 184.7 (CO), 166.4 (CN), 151.7, 151.6, 151.4, 151.0 (C̲-C-CH$_2$), (CH-N not resolved), 143.3 (C-Ir), 140.7, 140.4, 140.3, 139.9 (ArC), (C̲H-CH-CH-N not resolved), 126.9, 126.7, 126.1, 126.0, 125.9, 122.8, 121.4, 119.9, 119.8, 119.7 (CH), 100.8 (C̲H-CO), 55.3, 55.12, 55.06 (C̲-CH$_2$), 40.5, 40.3 (C-C̲H$_2$), 31.7, 31.4, 30.1, 30.0, 29.6, 29.2, 29.1 (CH$_2$), 28.7 (C̲H$_3$-CO), 23.9, 23.7 (C-CH$_2$-C̲H$_2$), 22.53, 22.51 (CH$_3$-C̲H$_2$), 14.0, 13.9 (CH$_3$). Mass (IE) m/z: 2819 (m, [M]$^+$), 2719 (w, [M–(acac)]$^+$). C$_{193}$H$_{247}$IrN$_2$O$_2$: calcd. C 82.22, H 8.83, N 0.88; found C 81.93, H 8.77, N 1.10.

Synthesis of ppy-pf8-ppy **Q**: Poly-Suzuki reaction of 9,9-di-n-octylfluorene containing 2-(6-p-pyridyl-phenyl) endgroups on both sides

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To a solution of 500 mg (0.78 mmol) of 2,7-di(4,4,5,5,-tetramethyl-1,3,2,-dioxaboronate)-9,9-dioctylfluorene, 405.5 mg (0.740 mmol) of 2,7-dibromo-9,9-dioctylfluorene and 17.1 mg (0.078 mmol) 2-(6-p-pyridyl-phenyl in 3 ml toluene was added: 4 mg (0.004 mmol) Pd(PPh$_3$)$_4$ and 2.5 ml of (3.1 mmol) Et$_4$NOH. The resulting mixture was stirred for 24 h at 100°C. After 3h, 5 ml toluene was added to dissolve the precipitated oligomers or to rise the viscosity of the mixture. After the mixture was cooled down to 20°C the mixture was slowly transferred in a large excess of MeOH, allowing the polymer to precipitate as a white (slightly greenish) fibre-like solid. The solids were collected on a filter, redissolved in 50 ml of toluene and subsequently filtered on a short column of silica. The filtrate was transferred into MeOH resulting in a reprecipitation of the polymer as off-white fibres. The solvents were removed under reduced pressure. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.72 (br d, 2H*12%; CH-N), 8.13 (br d, 2H*12%, CH-CH-CH-N), 7.9-7.5 (br, 6H, ArH), 2.3-2.0 (br, 4H, CH$_2$-C, 1.3-1.0 (br, 20H, CH$_2$), 0.9-0.7 (br, 10H, CH$_3$+CH$_2$). Mw (NMR): 10.000 (24-mer) GPC: Mp 48586, Mn 18618, Mw 67120, polydispersity 3.6.

Synthesis of ppy-pf8 E Suzuki polymerisation of 9,9-di-n-octylfluorene containing 2-(6-p-pyridyl-phenyl) endgroup on one side.
To a solution of 500 mg (0.56 mmol) of 2-(4,4,5,5,-tetramethyl-1,3,2,-dioxaboronate)-7-bromo-9,9-dioctylfluorene and 13.1 mg (0.056 mmol) 2-(6-p-pyridyl-phenyl in 5 ml toluene was added: 4 mg (0.004 mmol) Pd(PPh$_3$)$_4$ and 2.5 ml (3.1 mmol) of a Et$_4$NOH solution in water. The resulting mixture was stirred for 24 h at 110°C. After the mixture was cooled down to 20°C the mixture was slowly transferred in a large excess of MeOH, allowing the polymer to precipitate as a yellow-white solid. The solids were collected on a filter, redissolved in 50 ml of toluene and subsequently

filtered on a short column of silica. The filtrate was transferred into MeOH resulting in a reprecipitation of the polymer as off-white fibres. The solvents were removed under reduced pressure. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.75 (br d, 2H*12%; CH-N), 8.13 (br d, 2H*12%, CH-CH-CH-N), 7.9-7.5 (br, 6H, ArH), 2.3-2.0 (br, 4H, CH$_2$-C, 1.3-1.0 (br, 20H, CH$_2$), 0.9-0.7 (br, 10H, CH$_3$+CH$_2$). Mw (NMR): 5000 (12-mer).

Synthesis of R$_1$; [Ir(acac)(ppy-pf8-ppy)$_2$Ir(acac)]$_n$ via the iridium complexation of Q. A mixture of 200 mg Q (containing 0.159 mmol 2-(6-p-pyridyl-phenyl) and 12.5 mg IrCl$_3$ (containing 0.0353 mmol of iridium) was transferred in a solvent mixture of 5 ml of toluene and 3 ml of 2-ethoxyethanol. The resulting clear brownish mixture was heated to 100°C for 24 h and an orange gel was obtained which further precipitated in a large excess of MeOH. The product was collected on a glass fritted filter, washed with H$_2$O, MeOH and acetone, and finally the solvents were removed under reduced pressure. Subsequetly, a suspension of 161 mg of this product, with 20 mg (0.2 mmol) acetylacetone and 20 mg (0.19 mmol) of Na$_2$CO$_3$ in 5 mL of 2-ethoxyethanol and 10 mL of toluene was heated at 90°C for 24 h. After the reactionmixture was cooled down to roomtemperature the polymer was precipitated in a large excess of MeOH, collected on a filter and washed with H$_2$O, MeOH and acetone. The polymer was redissolved in 30 mL toluene upon heating at 90°C for 4 h. The resulting mixture was first filtered over glasswool and then over a short silica column after which the polymer was reprecipitated using MeOH. The resulting polymer shows remarkable low solubility in most common solvents; it was found soluble in toluene, dichloromethane and benzene only after lengthy solication. Yield: 161 mg. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.9-7.5 (br, 6H, ArH), 2,3-2.0 (br, 4H, CH$_2$-C), 1.3-1.0 (br,

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20H, CH$_2$), 0.9-0.7 (br, 10H, CH$_3$+CH$_2$) (signals of iridiumcomplex not resolved). Microanalysis: C 84.58, H 10.18, N 0.42, Ir (AES) 0.65.

Synthesis of R$_2$; [Ir(acac)(ppy-pf8-ppy)$_2$Ir(acac)]$_n$ via a poly-Suzuki reaction of 2,7-di(4,4,5,5,-tetramethyl-1,3,2,-dioxaboronate)-9,9-di-n-octylfluorene, 2,7-dibromo-9,9-dioctylfluorene and N (Ir(2(4-bromophenyl)pyridine)$_2$acac)

A solution of 500 mg (0.779 mmol) 2,7-di(4,4,5,5,-tetramethyl-1,3,2,-dioxaboronate)-9,9-dioctylfluorene, 405.5 mg (0.740 mmol) of 2,7-dibromo-9,9-dioctylfluorene, 29.5 mg (0.0389 mmol) of M (Ir(2(4-bromophenyl)pyridine)$_2$acac) and 4 mg (0.004 mmol) of (Pd(PPh$_3$)$_4$) in 10 mL of toluene was heated to 90°C and 2.5 mL (3.1 mmol) of a Et$_4$NOH solution in water was added. The resulting two-phase mixture was stirred for 18 h at 100°C and formed a brown-orange gel. The gel was precipitated in MeOH and washed with MeOH. The polymer was redissolved in 30 mL of dichloromethane and the resulting mixture was filtered using glass wool and subsequetly filtered over a short silica column. The resulting polymer is soluble in toluene and dichloromethane after lengthy sonication, and gives high viscosity. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 8.2-7.6 (br, 6H, ArH), 2,6-1.9 (br, 4H, CH$_2$-C), 1.6-0.7 (br, 30H, CH$_2$+CH$_3$) (spectrum is very broad, signals of iridiumcomplex not resolved). GPC: Mp 50643, Mn 28146, Mw 62638, polydispersity 2.2. Microanalysis: C 84.28, H 9.71, N 0.37, Ir (AES) 2.56.

Synthesis of S$_1$; [Ir(ppy-pf8)$_2$(acac)] via iridium complexation of E

A mixture of 150 mg E (containing 0.0367 mmol 2-(6-p-pyridyl-phenyl)) and 5.2 mg IrCl$_3$ (containing 0.0147 mmol of iridium) was transferred in a solvent mixture of 10 ml of toluene and 10 ml of 2-ethoxyethanol. The resulting clear yellow-orange

mixture was heated to 110°C for 24 h after which the product was precipitated in a large excess of MeOH. The product was collected on a glass fritted filter, washed with MeOH and hexane, and finally the solvents were removed under reduced pressure. Subsequetly, a clear solution the product and 20 mg (0.2 mmol) acetylacetone and 20 mg (0.19 mmol) of Na_2CO_3 in 8 mL of 2-ethoxyethanol and 2 mL of toluene was heated at 110°C for 2 h. Upon cooling to 0°C a yellow-orange precipitate was formed that was collected on a glass frittet filter, washed with H_2O and MeOH and the solvents were removed under reduced pressure. The product was filtered over a short silica column using toluene as the solvent. Yield: 100 mg. ^1H NMR (250 MHz, $CDCl_3$): δ = 8.65 (br, 1H*1%; CH-N), 7.9-7.5 (br, 6H, ArH), 6.62 (br, 1H*1%, CH-CHN), 5.30 (br, 0.5H*1%; CH-CO), 2.3-2.0 (br, 4H, CH_2-C), 1.82 (br, 3H*1%, CH_3-CO), 1.3-1.0 (br, 20H, CH_2), 0.9-0.7 (br, 10H, CH_3+CH_2). Microanalysis: C 83.09, H 9.61, N 0.39.

Synthesis of S_2: [Ir(ppy-pf8)$_2$(acac)] via a poly-Suzuki reaction using C 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-7-bromo-9,9-dioctylfluorene and M (Ir(2(4-bromophenyl)pyridine)$_2$acac)

A solution of 415 mg (0.697 mmol) of C, 26.4 mg (0.0349 mmol) of N, 2 mg (0.008 mmol) of Pd(acetate) and 4 mg (0.016 mmol) of PCy$_3$ was heated to 90°C and 2.5 mL (3.1 mmol) of a Et$_4$NOH solution in water was added. The resulting mixture was stirred at 110°C for 20 h, resulting in a slightly viscous clear red solution. The organic layer was dropped out in a large excess of MeOH, which resulted in the precipitation of an orange polymer. This was washed with water, MeOH and acetone and filtered over a short silica column using toluene as the eluent. The resulting solution was concentrated to 2 ml and 100 mg of Na_2CO_3, 1 mL of acacH and 8 mL of 2-

ethoxyethanol were added. The reactionmixture was stirred for 2 h at 110°C and subsequently cooled down to roomtemperature. 2 mL of MeOH was added on which the product precipitated as an orange solid. The product was isolated on a glass fritted filter, washed with H_2O and MeOH and the solvents were removed under reduced pressure. Yield: 150 mg (55%). δ = 8.7 (d, J = 4.6 Hz, 1H*10%; CH-N), 7.9-7.5 (br, 6H; ArH), 7.4-7.1 (br, ArH), 6.6 (s, 1H*10%; C$\underline{H}$-CH-N), 5.3 (s, 0.5H*10%; CH-CO), 2.3-2.0 (br, 4H, CH_2-C), 1.9 (3H*10%; CH_3-CO), 1.3-1.0 (br, 20H, CH_2), 0.9-0.7 (br, 10H, CH_3+CH_2). Microanalysis: C 82.78, H 9.44 , N 0.25.

S_3 was synthesised analogues to S_2 but using a solution of 415 mg (0.697 mmol) of C and 13.2 mg (0.0349 mmol) of N. Yield: 230 mg (85%). δ = 8.7 (d, J = 5.0 Hz, 1H*3%; CH-N), 7.9-7.5 (br, 6H; ArH), 7.4-7.1 (br, ArH), 6.6 (s, 1H*3%; C$\underline{H}$-CH-N), 5.3 (s, 0.5H*3%; CH-CO), 2.3-2.0 (br, 4H, CH_2-C), 1.9 (3H*3%; CH_3-CO), 1.3-1.0 (br, 20H, CH_2), 0.9-0.7 (br, 10H, CH_3+CH_2). Microanalysis: C 87.10, H 10.02 , N 0.20.

LED fabrication and measurements

The electroluminescent devices have been fabricated as described below. An indium–tin oxide (ITO) patterned and cleaned glass substrate was obtained from Cambridge Display Technology Limited. A hole-injection layer, Poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS, obtained from Bayrton as an aqueous solution and used without further pretreatment), was spin-coated (2000 rpm, 30 seconds) onto the ITO. The PEDOT:PSS layer was dried on a hotplate (130 C) for 5 minutes. Next, a hole-transport layer of polyvinylcarbazole (PVK) was spin-coated, from a 3 mg/mL solution in dichloromethane, on top of the PEDOT:PSS layer. Subsequently, the light-emitting polymer was spin-coated (from a 10-15 mg/mL solution in toluene) on top of this layer. Then, the device was transferred to a high-vacuum (1 × 10^{-5} mbar) deposit unit and set with a shadow mask. A cathode metal, calcium, was deposited on the organic layers through the shadow mask, followed by deposition of aluminium. The size of each pixel is 4 mm × 3.2 mm. The device was

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finally encapsulated using Araldite epoxy resin and covered with a glass slide. Typical characteristics of the device layers include: ITO (190 nm, sheet resistance < 10 Ω/) / PEDOT:PSS (50 nm) / PVK (45 nm)/ light-emitting polymer (70 nm) / Ca (40 nm) / Al (200 nm). The devices were examined by applying a direct current bias (0 to 25 V) to the electrodes. The electroluminescent characteristics were measured with a Hewlett-Packard E3631A DC Power Supply, Keithley 2000 Digital Multimeter, Topcon BM-9M Luminance Meter, and Aminco-Bowman Series 2 Fluorescence Spectrometer.

Results and Discussion

Synthesis of iridium(ppy)-fluorenyl hybrid systems

The 4-position of 2-phenylpyridine (ppy) was functionalised with a series of 9,9-dialkylfluorene segments including one, two and three subsequent fluorenyl substituents (Scheme 1).

Scheme 1: Synthetic pathway to 9,9-dialkylfluorene substituted 2-phenylpyrine ligands

(2(4-bromophenyl)pyrine) (**A**) was synthesised via a coupling of pyridine to parabromoaniline using the Gomberg-Hey reaction.[19] Monofluorenyl functionalised ppy was obtained by a Suzuki coupling of **A** with 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-9,9-dihexylfluorene to obtain (2-(6-p-pyridyl-phenyl)-9,9-dihexylfluorene) (**D**). The key building block of our stepwise synthesis; 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-7-trimethylsilyl-9,9-dioctylfluorene (**B**) was synthesised in two steps from 2,7-dibromo-9,9-dioctylfluorene via a monolithiation using nBuLi, quenched with TMSCl followed by a second lithiation using tBuLi, that was further reacted with 2- isopropoxy-4,4,5,5 tetramethyl-1,3,2-dioxaborolane to

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obtain **B**. 4-Difluorenyl functionalised ppy was obtained in two steps from the Suzuki product of **A** and **B** via the deprotection of the TMS group using ICl (which yields 2-(6-p-pyridyl-phenyl)-7-tetramethyl-1,3,2-dioxaborolane)-9,9-dihexylfluorene to obtain 2-(6-p-pyridyl-phenyl)-7-(9,9-dihexylfluorenyl)-9,9-dioctylfluorene (**H**).[20] 4-Trifluorenyl functionalised ppy was obtained from the Suzuki product of **G** and 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-9,9-dihexylfluorene via the same deprotection/Suzuki reaction sequence to obtain 2-(6-p-pyridyl-phenyl)-7-(2-(7-[2-(9,9-dihexylfluorenyl)]))-9,9-dioctylfluorenyl)-9,9-dioctylfluorene (**K**).

Scheme 2: Synthesis of 4-fluorenyl functionalised ppy ligands

Oligofluorene-bis-ppy was synthesised using a Pd(PPh₃)₄ catalysed poly-Suzuki reaction using **A**, 2,7-di(4,4,5,5,-tetramethyl-1,3,2,-dioxaboronate)-9,9-dioctylfluorene and 2,7-dibromo-9,9-dioctylfluorene as the building blocks to yield ppy-pf8-ppy (**Q**) (Scheme 2).[21] Oligofluorene-mono-ppy was obtained from the same coupling reaction using **A** and 2-(4,4,5,5 tetramethyl-1,3,2-dioxaborolane)-7-bromo-9,9-dioctylfluorene (**C**) as the building blocks to obtain ppy-pf8 (**E**) (Scheme 2).

Bis-cyclometalated iridium complexes of the type Ir(ppy-X)₂(acac) were synthesised according to a two-step synthetic route that was recently reported by Lamansky et al.[22] In the first step, IrCl₃.nH₂O is reacted with an excess of the ppy containing ligand to yield the chloro-bridged dimer [Ir(ppy-X)₂(-μ-Cl)]₂ (Scheme 3)

Scheme 3: Synthesis pathway to bis-CN-cyclometalated iridium complexes

The chloro-bridges iridium dimers are subsequently converted to phosphorescent monomeric acetylacetonate complexes. (Ir(2(4-bromophenyl)pyridine)$_2$acac) **(M)**, (Ir(2-(6-p-pyridyl-phenyl)-9,9-dihexylfluorene)$_2$(acac)) **(N)**, (Ir(2-(6-p-pyridyl-phenyl)-7-(9,9-dihexylfluorenyl)-9,9-dioctylfluorene)$_2$(acac)) **(O)**and Ir(2-(6-p-pyridyl-phenyl)-7-(2-(7-[2-(9,9-dihexylfluorenyl)]))-9,9-dioctylfluorenyl)-9,9-dioctylfluorene)$_2$(acac)) **(P)** were all synthesised accordingly (Scheme 3).

The synthesis of iridium(ppy)-oligofluorenyl systems was attempted via two approaches (Scheme 4).

Scheme 4: Synthetic pathways towards Ir(ppy)-oligofluorenyl systems

Analogous to the model compounds, both **Q** and **E** were exposed to the two-step synthetic pathway via the chloro-bridged iridium dimer towards the acetylacetonate containing monomer. This seemed troublesome using **Q**, since a full conversion to the chloro-bridged idirium dimer was frustrated by gellation of the reactionmixture. AES analyses on the targeted product; [Ir(acac)(ppy-pf8-ppy)$_2$]$_n$ **(R$_1$)** revealed that the iridium content was only 0.65% (objected: 4%). Moreover, the resulting polymer did only dissolve after extensive sonication. Upon complexation of **E** the gel-formation was completely avoided due to the prevention of network formation of the dichloro-bridged intermediate. Hence, the product of this two-step reaction sequence; [Ir(ppy-pf8)$_2$(acac)] **(S$_1$)** is readily soluble in dichloromethane and toluene. From NMR it was concluded that 1% Ir(ppy)$_2$(acac) segments are present (while 4% was objected).

Alternatively, complex **M** was applied in a poly-Suzuki reaction using 2,7-di(4,4,5,5,-tetramethyl-1,3,2,-dioxaboronate)-9,9-dioctylfluorene and 2,7-dibromo-

9,9-dioctylfluorene as the building blocks to yield [Ir(acac)(ppy-pf8-ppy)$_2$]$_n$ (R$_2$).

Also via this pathway the synthesis of R gave rise to gelformation during the reaction and caused solubility problems in the manufactoring of it. This method did however give rise to an increased inbuild of Ir(ppy)(acac) segments compaired to approach R$_1$; in this case the iridium contents was 2.6%. The most successful iridium(ppy)-oligofluorenyl system was obtained via a poly-Suzuki reaction using C and M. The resulting product [Ir(ppy-pf8)$_2$(acac)] (S$_2$) was highly soluble in dichloromethane and toluene and contained 5% of the bis-cyclometalated iridium complex. A subsequent reaction with acacH was needed to restore the acac-anion back on the complex.

Photophysical properties of Ir(ppy-X)$_2$(acac) complexes

Absorption and photoluminescence (PL) spectra were recorded of the series of cyclometalated iridium complexes to investigate the influence of the fluorenyl-substitution on the 4-position of the ppy (Figure 1).

Figure 1: Absorption and PL-spectra of Ir(ppy-X)$_2$(acac) complexes

The parent compound L shows an *absorption* band and 260 nm while it emits at 507 nm. When a monofluorenyl-segment is placed at the 4 position of the ppy (complex N), the absorption maximum was observed at 338 nm with a second, minor maximum at 260 nm. Clearly, complex N absorbs both from the aromatic π system as well as from the d-orbitals of the iridium complex. Further extension of the aromatic system of the ligands with subsequent fluorenyl units (via complexes O and P) resulted in a red shift of the absorption maximum from the aromatic π system of the ligand accompanied by a relative decrease of the absorption intensity originating from the transition metal. Complex P shows a maximum absorption at 376 nm which is

only 8 nm lower than where polyfluorene absorbs. For this complex, the absorption from the transition metal is only observed as a minor absorption peak at 260 nm. In comparison; when the 4-position of the ppy was substituted by a bromine, it had no impact on the absorption spectrum at all.

Interestingly, compared to the unsubstituted complex, the *PL-spectrum* of complex **N** (one fluorenyl) is red shifted with respect to **L** by 30 nm, to 552 nm. From this it can be concluded that the triplet wavefunction in this system is not confined to the Ir(ppy) unit but extended over the complete aromatic system. A second fluorenyl-segment (complex **O**) gave rise to a further red shift of 9 nm (to 561 nm) and a third (**P**) provided a PL-maximum of 566 nm.

In general it appears that the influence of the repeat units of the fluorenyl-chain on the wavefunction is gradually decreasing when positioned further away from the phosphor, but that at least the first three fluorenyl units influence the triplet wavefunction (in our case by causing a total red shift of 44 nm).

EL-characteritics were investigated by manufactoring OLED's (organic light emitting diode) from these model compounds. The OLED device consists of a basic three layered structure sandwiched between indium tinoxide and a calcium electrode; ITO/PEDOT-PSS/PVK/Emitting layer/Ca/Al. The use of PEDOT-PSS is commonly known as a hole-injection layer, the polyvinylcarbazole layer (PVK) is added as a hole transport layer and was found to generally smoothen the device characteristics. The series of **L**, **N**, **O** and **P** were spincoated in this structure from a toluene solution. The EL-spectra of these devices roughly show the same trend as the PL-spectra. In this series, the emission maximum shifts red from 529 nm for **L**, via 561 nm (**N**), to 567 nm for **O** and **P**. Apart from a little red-shift all of the EL-spectra of these

compunds closely resemble their PL-spectra. Not a trace of fluorenyl originating singlet emission from these systems was observed.

Figure 2: EL spectra of Ir(ppy-X)$_2$(acac) (inset shows the device structure)

Table 1: EL-characteristics of Ir(ppy-X)$_2$(acac)

System	Lum. max (cd/m²)	turn on voltage (V)	CIE X	CIE Y	Efficiency (cd/A)	ELQY (%)	Colour
L	60	4.0	0.37	0.59	$2.5*10^{-3}$	$7.4*10^{-4}$	yellowish-green
N	43	5.0	0.48	0.51	$9.9*10^{-3}$	$3.3*10^{-3}$	greenish yellow
O	400	5.5	0.48	0.51	$6.9*10^{-2}$	$2.2*10^{-2}$	yellow
P	1400	6.0	0.46	0.53	$7.3*10^{-2}$	$7.3*10^{-2}$	greenish yellow

The device properties improve substantially on extending the ligand system with fluorenyl segments (Table 1 and Figure 3). The maximum brightness increased from 60 (for **L**), via 43 for **N**, 400 for **O** to 1400 for **P**, while the quantum yield improved two orders of magnitude from $7.4*10^{-4}$ to $7.3*10^{-2}$.[23] The turn on voltage went up slightly upon increasing the percentage of fluorene.

From the experiments described above it was concluded that the covalent bonding of fluorenyl segments directly to the aromatic system of the ligand system of this type of phosphorescent complexes is benificial for its ability to harvest triplets. This phenomenon is not explained solely by the improved film formating capabilities of the higher fluorenyl substituted phosphors. We suggest that upon increasing the aromatic system of the phosphor, more uniform films are obtained with a more homogeneous distribution of the iridium(ppy) species, avoiding clustering which can give rise to triplet annihilation. The size of the aromatic system of the phosphors might also be of importance in the efficiency of capturing charges.

Figure 3: I-L-V curves of Ir(ppy-X)₂(acac)

The results propted us to investigate this type of phosphors in a polyfluorene matrix. PL measurements of blends of complex **L** and **N** in a 9,9-dioctyl-polyfluorene (PF8) matrix revealed that singlet emmision from the polyfluorene was significantly quenched by both phosphors, but that the triplet emission (at roomtemperature under airobic conditions) from both systems was very low (Figure 4). Exciton *Föster* transport from the S_1 of the polymer to the T_1 seems to be efficient, but a different mechanism (triplet annihilation, or *Dexter* transfer of triplets from the phosphor back to the polymer) seems responsible for a major quenching of excitons on the phosphor.

Figure 4: PL spectra of blends of complex N in PF8. Inset; triplet signal of blends of 5.0 mol % of complex L and N in PF8

The EL spectrum of **L** in PF8 showed a marked resemblance with that of undoped PF8, but the emission maximum was shifted from 516 to 533 (note that the emmision maximum of 516 nm of PF8 is caused by eximer formation due to aggregation effects) (Figure 5). It seems that this device emits both from the singlet excited state of the polymer (a maximum at 414 nm) as well as from the triplet excitons in the transition metal complex (533 nm). The blend of complex **N** in PF8 showed nearly only triplet emission. The emission maximum at 559 nm is clearly originating from the phosphor (552 nm was observed for the neat complex; Figure 2) whereas the singlet peak at 443 nm is very small. We owe this difference between complex L and

Figure 5: EL spectra of Ir(ppy-X)₂(acac) in polyfluorene

N to the difference in T_1-level. From the emission spectra it was estimated that the T_1-level of L is about 2.4 eV, and that of complex N is 2.2 eV. On comparing this with the T_1 level of PF8, which is recently calculated to be about 2.30 eV[24] it can be predicted that in the case of L part of the triplets, captured on the phosphor, will hop to the T_1-level (*Dexter* transfer) of the polymer and decay non-radiatively. Hence triplet emmision is frustrated by this process. In the case of complex N such a process is less likely since the estimated T_1-level of the polymer is higher than that of the phosphor.

Table 2: EL-data on blends of Ir(ppy-X)$_2$(acac) in polyfluorene

System	Lum. max (cd/m^2)	turn on voltage (V)	CIE X	CIE Y	Efficiency (cd/A)	ELQY (%)	Colour
L in PF8	225	5.5	0.35	0.48	0.16	$7.6*10^{-2}$	yellowish-green
N in PF8	190	7.5	0.44	0.52	0.15	$5.6*10^{-2}$	greenish yellow

The enhanced triplet to singlet ratio of complex N in PF8, compared to the blend of L, doesn't give rise to a significant change in device efficiency ($5.6*10^{-2}$ vs $7.6*10^{-2}$, Table 2).

Polyfluorenyl functionalised phosphors

The concept of fluorenyl substituted phosphors was taken one step further by implimentating the bis-cyclometalated iridium phosphors in the main chain of polyfluorene. The PL-spectra of these hybrid systems (R_1, R_2, S_1, and S_2) are depicted in Figure 6.

Figure 6: PL-spectra of Ir(ppy-X)$_2$(acac) incorporated polyfluorenes

All systems show singlet emission (with maxima at 422 and 450 nm) originating from the polyfluorene part of the molecule. In R_1 and R_2 no triplet emission was observed. This, together with the NMR-spectra, strongly suggests that in these systems the Ir(ppy-X)$_2$(acac) phosphor could no be adeqautely implemented in the polymer chain due to gelation problems during the synthesis. In this respect systems S_1 and S_2 were more promising since in these materials, only one phosphor can be build in every molecule (Scheme 4) leading to better defined and applicable (solluble) systems. Both S_1 and S_2 showed triplet PL-emission at 596 nm.

The EL-spectra of the novel hybrid system, depicted in Figure 7, again show the marked diffences between the R and S products.

Figure 7: EL-spectra of polyfluorene incorporated iridium-complexes

The spectra of R_1 and R_2 are very broad and show a lot of singlet and singlet-excimer emission, caused by aggregation (the low solubility of these compounds gave rise to increased aggregation, compared to normal polyfluorene). R_1 doesn't show any triplet emission at all, while a shoulder at ~ 604 nm could indicate some triplet emission from the device fabricated from system R_2. The device, containing system S_1 was found to emit singlets and triplets in the ratio 1:3 and S_2 yielded a singlet to triplet ratio of 1:23. This resulted in pink emission (according to the CIE-coordinates X = 0.42 and Y = 0.34) for S_1 systems whitish orange emmision for S_2 (X = 0.47 and Y = 0.43) (Table 3).

Figure 8: EL-spectra of S_2 at increasing driving voltage, going from 8.5V (bottom) up in steps of 0.5V to 12.5V (top).

The singlet to triplet ratio was found to increase upon increasing the driving voltage (Figure 8). This is explained by an increase in triplet-triplet anihilation at higher

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driving voltages. The observed increase in excimer formation at increased driving voltages is a wellknown phenomenon in polymer LED's.

Table 3: EL-data on polyfluorenyl-iridium(ppy) complexes

System	Lum. max (cd/m^2)	turn on voltage (V)	CIE X	CIE Y	Efficiency (cd/A)	ELQY (%)	Colour
R_1	10	8.5	0.29	0.45	$7.0*10^{-2}$	$2.6*10^{-2}$	yellowish-green
R_2	60	8.5	0.33	0.44	0.13	$7.1*10^{-2}$	yellowish-green
S_1	42	9.5	0.42	0.34	$7.6*10^{-2}$	$3.6*10^{-2}$	pink
S_2	163	7.0	0.47	0.43	0.19	$7.9*10^{-2}$	whitish-orange
S_3	304	6.0	0.42	0.40	0.18	$7.9*10^{-2}$	whitish-orange

The EL-device characteristics of the hybrid systems are summarized in Table 3. As observed from the EL-spectra the **R** samples give yellowish-green emission, originating from singlet- and singlet-excimer emission at low brighness (10 cd/m^2 for R_1 and 60 cd/m^2 for R_2) at a quantum yield of $2.6*10^{-2}$ and $7.1*10^{-2}$ respectively. The better defined S samples emit mainly from the triplet state and a little from the singlet excited state. S_1 gives pink emission (CIE-X 0.42, CIE-Y 0.34) with a maximum brightness of 42 cd/m^2 with a quantum yield of $3.6*10^{-2}$. S_2 ans S_3 both yield whitish orange emmision at a quantum yield of $7.9*10^{-2}$. The relative longer polyfluorene substituents of S_3 (30 fluorenyl units versus 10 for S_2) gives rise to an increase of the maximum brighness from 163 to 304 cd/m^2.
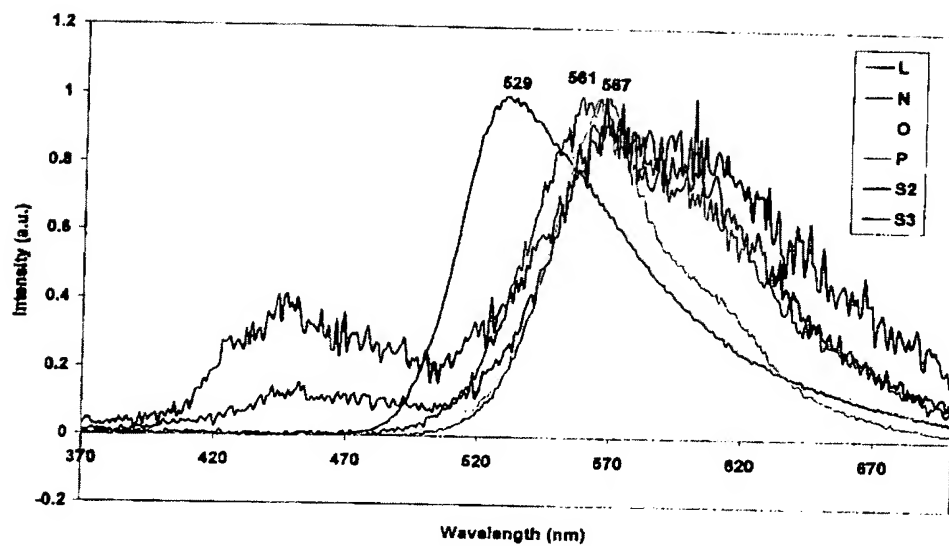
Conclusion

We have developed a series of polyfluorenyl-phosphor composite materials that give bright phosphorescence in solution-processed devices. The addition of fluorene

substituents to the ligands of the small molecule Ir(ppy)$_2$(acac) yielded materials that are readily spin-coated from solution of blends in fluorene and, more importantly, also as neat materials. The fluorenyl substituents were found to give rise to a major improvement in EL-luminance brightness and in quantum efficiency. A benificial effect of the substituents was observed in the improved complementation of the T$_1$- energy level of the phosphor to that of polyfluorene in blends. OLED's prepared from polyfluorenyl-phosphor composites were reported to yield bright triplet emitting devices. We believe that for large-area devices, like matrix displays, the manufactoring of these types of materials are very promissing. We certainly realize that our composites are far less efficient then the small molecule deposited devices, since the quantum yield of triplets in PLED's is far from optimal, as opposed to small molecule devices. Major improvent can be expected in the application of polymeric electrontransport and hole blocking materials to enable a better confinement of the excitons in the emitting layer.[25]
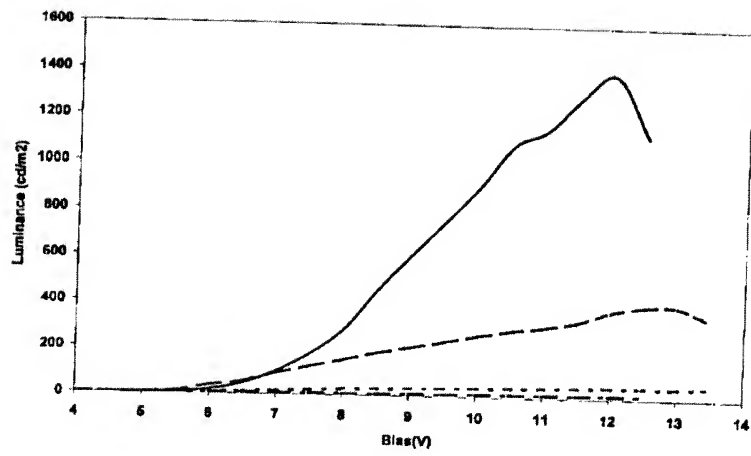
<Figure 1>

<Figure 2>

<Figure 3>

< Figure 4>

<Figure 5>

38

<Figure 6>

<Figure 7>

<Figure 8>

41

<Scheme 1>

42

< Scheme 2>

2 IrCl₃.H₂O + 4 [phenylpyridine] → [Ir(ppy)₂Cl]₂ dimer → (acacH/Na₂CO₃) → [Ir(ppy)₂(acac)]

X—[benzene-pyridine]₂—Ir(acac)   X = H (L), Br (M)

C₆H₁₃ C₆H₁₃   C₈H₁₇ C₈H₁₇   n = 0 (N), 1 (O), 2 (P), oligomer (Q)
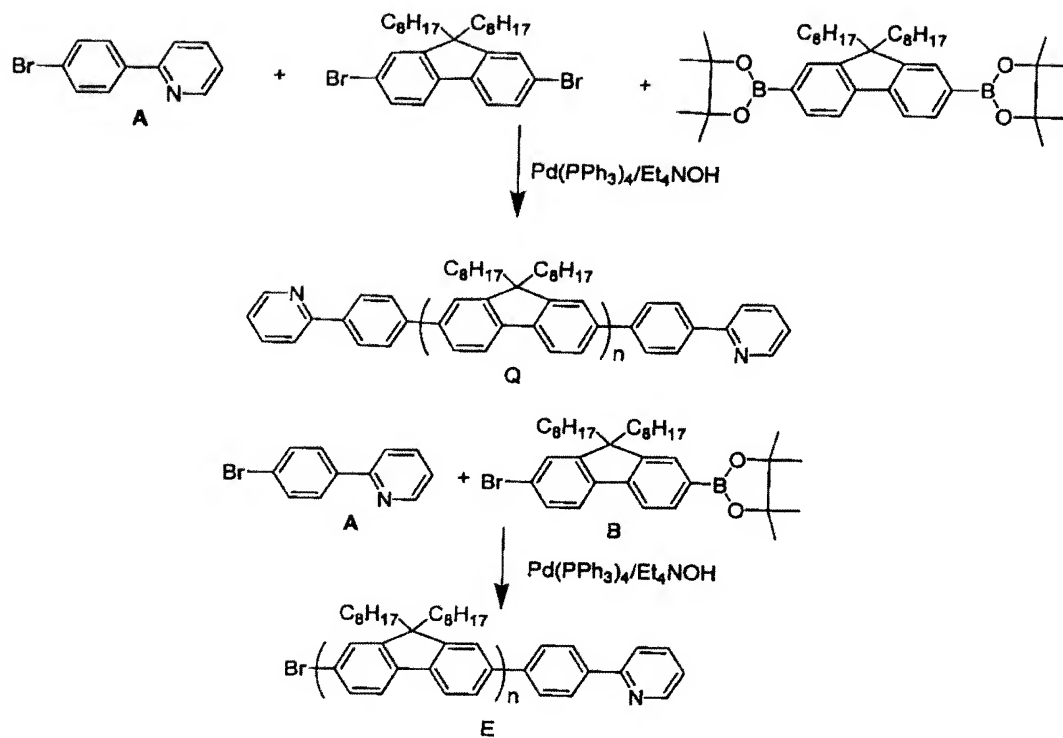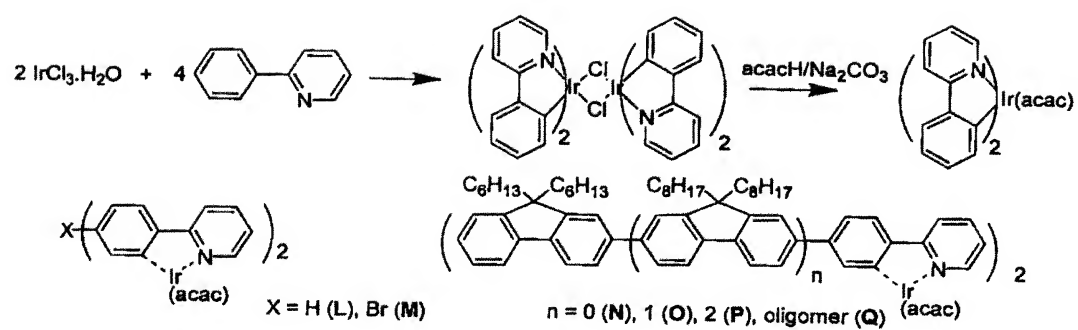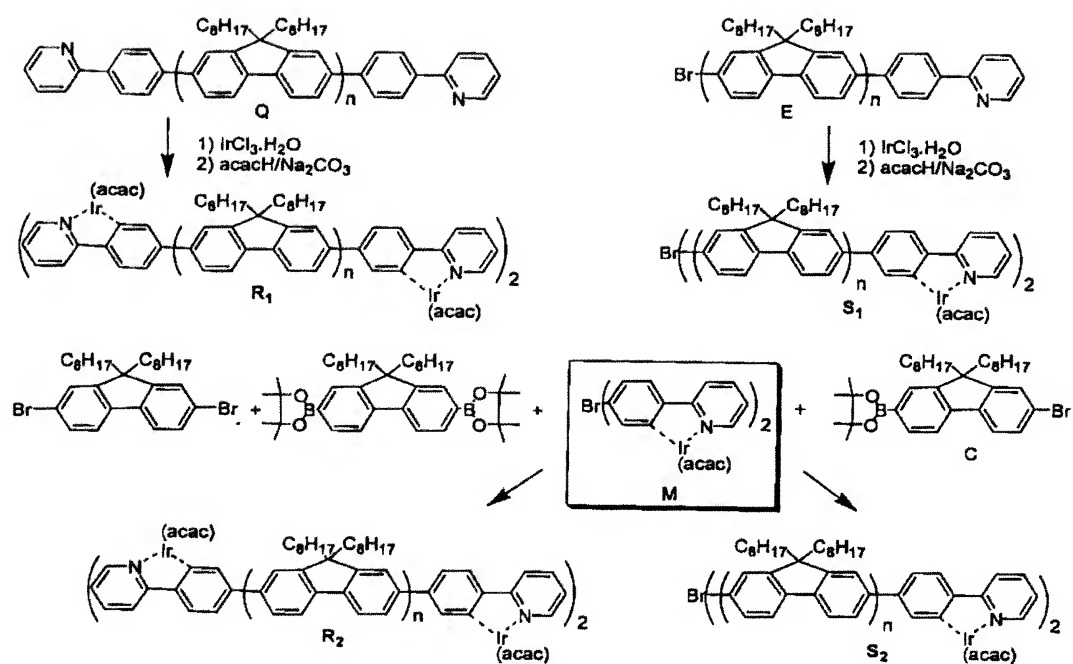
<Scheme 3>

44

<Scheme 4>

45
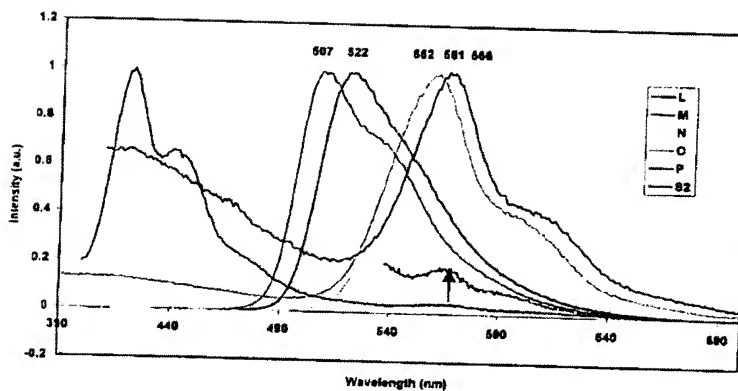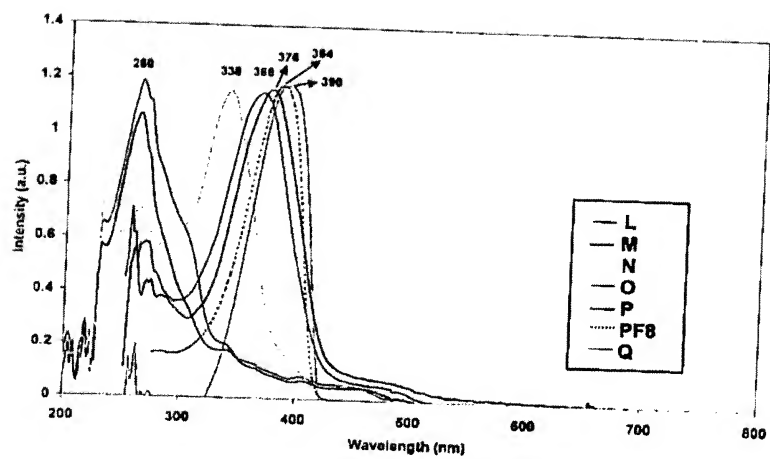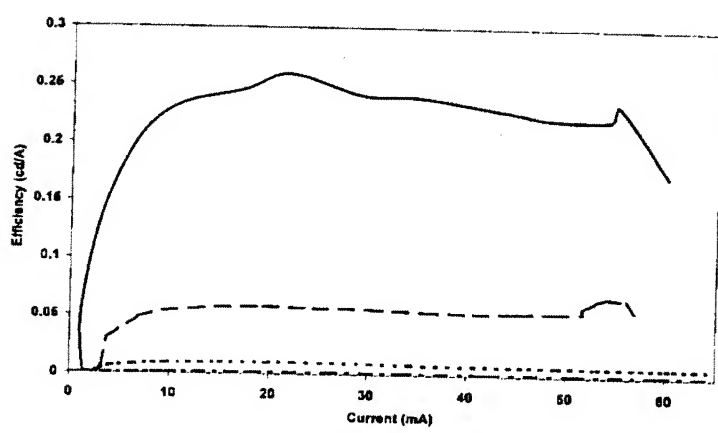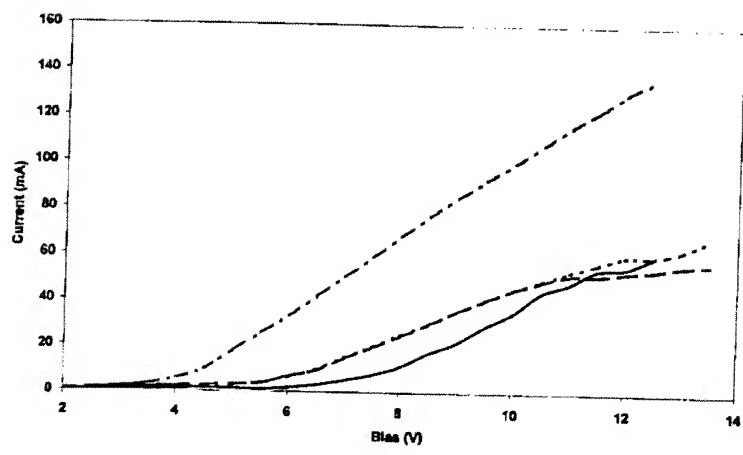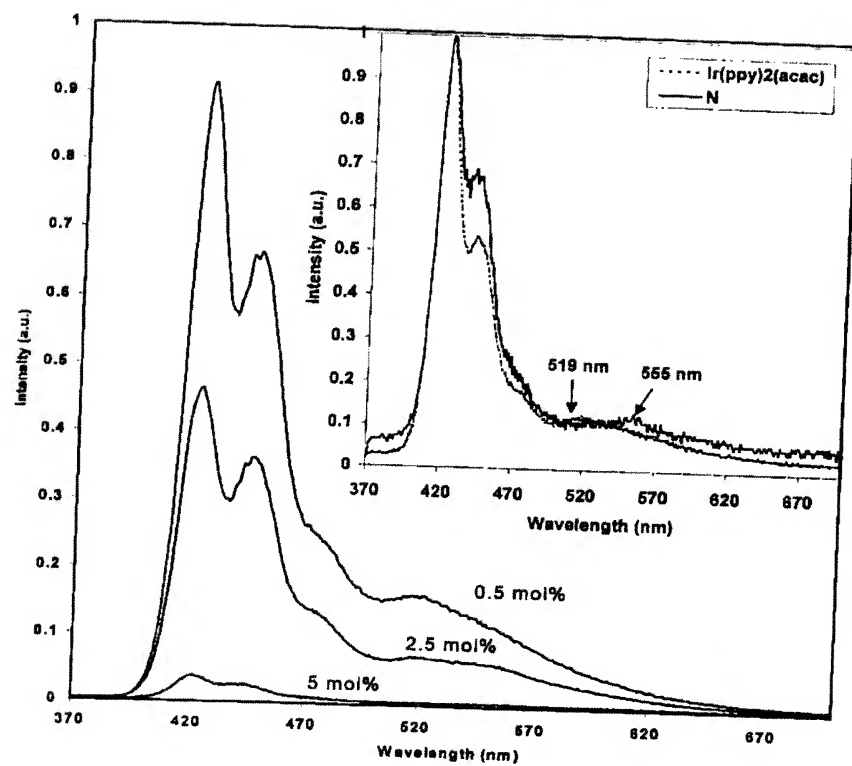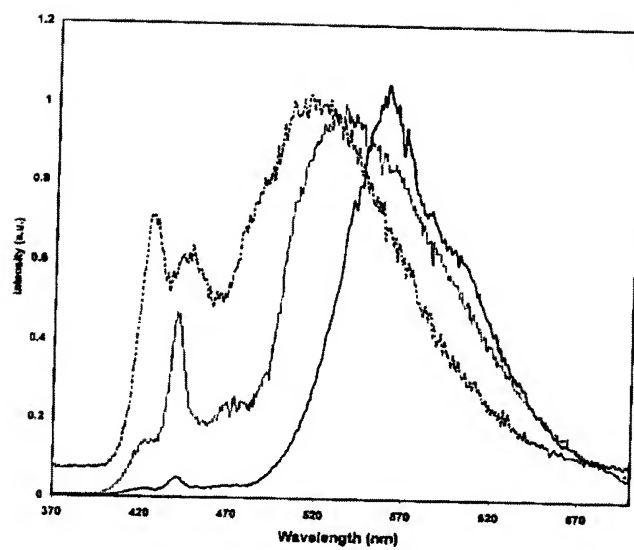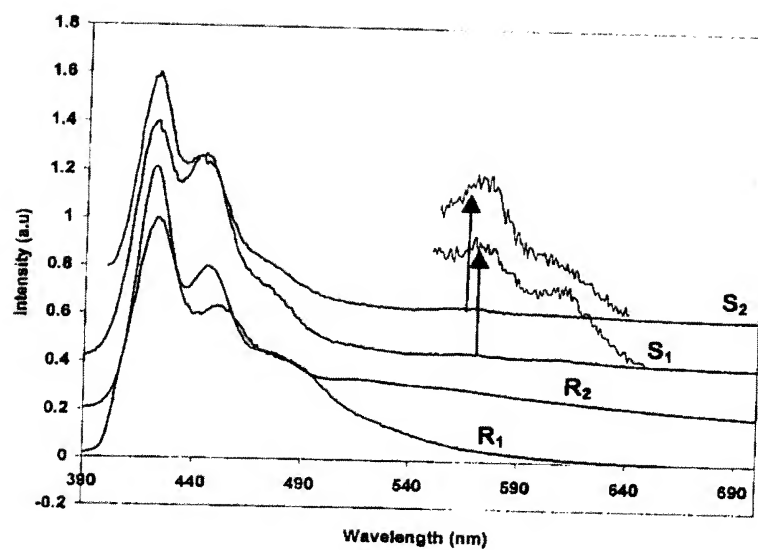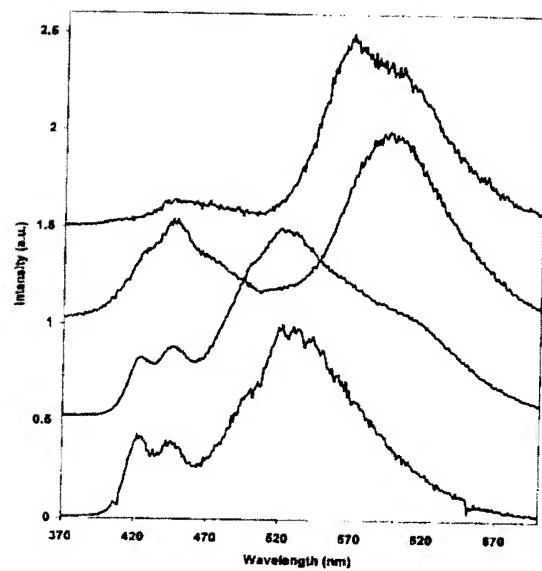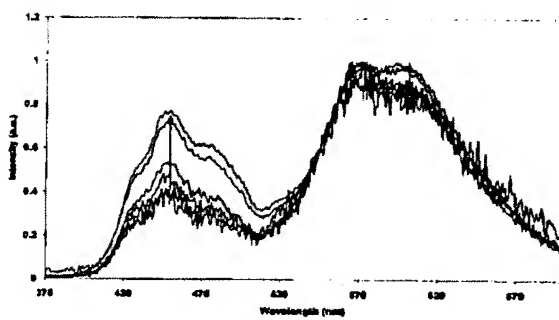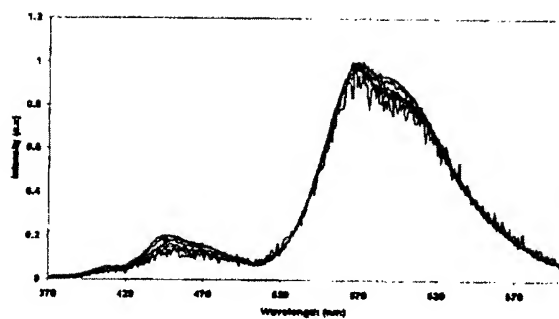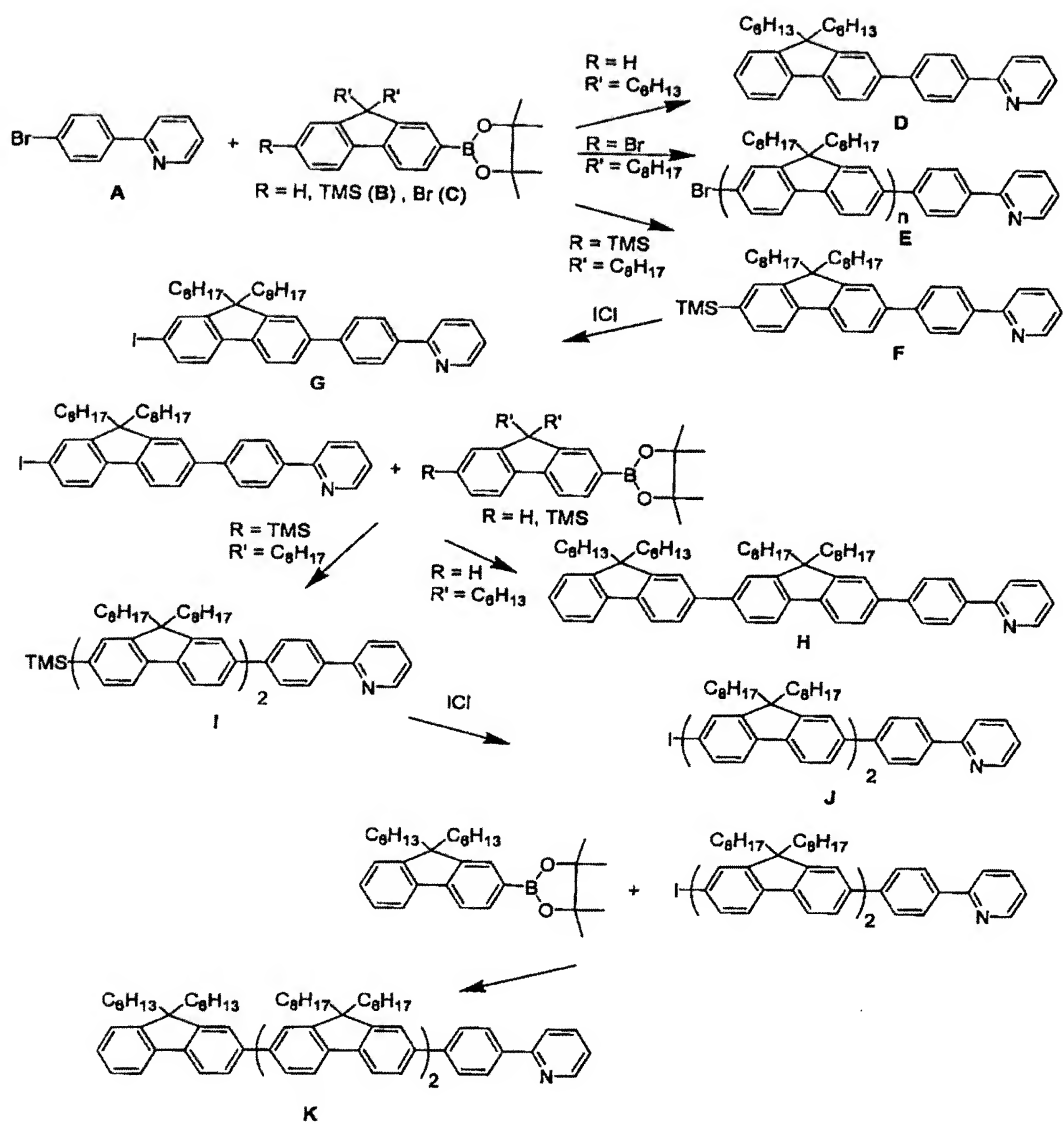
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